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(54) [Title of the Invention] ANTIREFLECTIVE MEMBER AND
MANUFACTURING METHOD THEREOF

(57) [Abstract]

[Object] It is an object of the present invention to provide an antireflective member for which adhesion of a low-refractive layer of the surface of the antireflective member with a lower hard-coat layer or with an upper high-refractive layer or the like has been improved, and to provide a manufacturing method thereof.

[Solving Means] A lamination structure comprises a substrate 2, a hard coat layer 3 and a low-refractive layer 4, or a substrate 2, a hard coat layer 3, a high-refractive layer 6 and a low-refractive layer 4 in this sequence. In a state in which the lower low-refractive layer is partially hardened, components of the composition for forming the low-

refractive layer are used for impregnation and hardened, thereby forming an antireflective member 1 comprising an impregnated portion 5A or 5B.

[Claims]

[Claim 1] An antireflective member having a lamination structure in which a hard coat layer and a low-refractive layer sequentially laminated which comprise a resin composition containing resins on a substrate; wherein a surface layer portion of said hard coat layer has an impregnated portion impregnated with components of said low-refractive layer.

[Claim 2] An antireflective member having a lamination structure in which a hard coat layer, a high-refractive layer or a conductive layer, and a low-refractive layer sequentially laminated which comprise a resin composition containing resins on a substrate; wherein the surface layer of said hard coat has an impregnate portion impregnated with components of said high-refractive layer or said conductive layer, and/or the surface layer of said high-refractive layer or said conductive layer has an impregnate portion impregnated with components of said low-refractive layer.

[Claim 3] An antireflective member according to claim 1 or 2, wherein said hard coat layer is composed of a thermosetting resin composition containing a thermosetting resin and/or a setting resin composition comprising a set material of an ionizing-radiation-setting resin composition containing an ionizing-radiation-setting resin.

[Claim 4] An antireflective member according to claim 2,

wherein said high-refractive layer is composed of a thermosetting resin composition containing a thermosetting resin and/or a setting resin composition comprising an ionizing-radiation-setting resin composition containing an ionizing-radiation-setting resin.

[Claim 5] An antireflective member according to claim 4, wherein said high-refractive layer further contains inorganic ultrafine particles.

[Claim 6] An antireflective member according to any one of claims 1 to 5, wherein said high-refractive layer has a refractive index over 1.46.

[Claim 7] An antireflective member according to any one of claims 1 to 6, wherein said low-refractive layer is composed of a thermosetting resin composition containing a thermosetting resin and/or a setting resin composition comprising a setting material of an ionizing-radiation-setting resin composition containing an ionizing-radiation-setting resin.

[Claim 8] An antireflective member according to claim 7, wherein said low-refractive layer contains a fluorine-containing polymer component.

[Claim 9] An antireflective member according to claim 7, wherein said low-refractive layer contains a fluorine-containing oligomer component.

[Claim 10] An antireflective member according to claim 7,

wherein said low-refractive layer contains a polysiloxane component.

[Claim 11] An antireflective member according to any one of claims 1 to 10, wherein said low-refractive layer has a refractive index of 1.10 to 1.46.

[Claim 12] A manufacturing method of an antireflective member for sequentially laminating a hard coat layer and a low-refractive layer both mainly comprising a resin composition on a substrate, comprising the steps of forming a hard coat layer not as yet completely set by causing partial setting through coating of a coating composition for forming a hard coat layer containing a resin on the substrate; laminating a low-refractive layer not as yet set by coating a coating composition for forming a low-refractive layer containing a resin on said hard coat layer not as yet completely set; after lamination, forming an impregnate portion in a surface layer of said hard coat layer by causing said hard coat not as yet completely set to be impregnated with said composition for forming the low-refractive layer in said low-refractive layer not as yet set; and then, causing hardening of the entire lamination thus formed.

[Claim 13] A manufacturing method of an antireflective member for sequentially laminating a hard coat layer, a high-refractive layer and a low-refractive layer, all mainly

comprising a resin composition on a substrate, comprising the steps of forming a hard coat layer by coating and causing setting of a coating composition for forming a hard coat layer containing a resin on the substrate; then, forming a high-refractive layer not as yet completely set by causing partial setting through coating of a coating composition for forming a high-refractive layer containing a resin on said hard coat layer; and thereafter, laminating an unset low-refractive layer by coating a coating composition for forming a low-refractive layer containing a resin on said high-refractive layer not as yet completely set; after lamination, forming an impregnate portion in a surface layer of said high-refractive layer by causing impregnation of said high-refractive layer not as yet completely set with said composition for forming the low-refractive layer in said unset low-refractive layer; and thereafter, causing setting of the entire lamination thus formed.

[Claim 14] A manufacturing method of an antireflective member for sequentially laminating a hard coat layer, a high-refractive layer and a low-refractive layer, all mainly comprising a resin composition on a substrate, comprising the steps of forming a hard coat layer not as yet completely set by coating and causing partial setting of a coating composition for forming a hard coat layer containing a resin on the substrate; then, laminating an unset high-refractive

layer by coating a coating composition for forming a high-refractive layer containing a resin on said hard coat layer not as yet completely set; after lamination, forming a first impregnate portion in a surface layer of said hard coat layer by causing impregnation of said hard coat layer not as yet completely set with said composition for forming a high-refractive layer in said unset high-refractive layer; and further thereafter, laminating an unset low-refractive layer by coating a coating composition for forming a low-refractive layer containing a resin on said high-refractive layer not as yet completely set; after lamination, forming a second impregnate portion in a surface layer of said high-refractive layer by causing impregnation of said high-refractive layer not as yet completely set with said composition for forming the low-refractive layer in said unset low-refractive layer; and thereafter, causing setting of the entire lamination.

[Detailed description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to an antireflective member having a lamination structure in which a low-refractive layer is laminated directly on a hard coat layer or via another layer, and having an improved adhesion between the hard coat layer and the low-refractive layer or between another layer provided

on the hard coat layer and the low-refractive layer. The present invention includes a laminating method of an antireflective member permitting improvement of adhesion between such individual layers.

[0002]

[Description of the Related Art] It is the common practice to maintain transparency of a glass plate, a plastic film and the like or to prevent reflection on the surface of various articles not having transparency by themselves. Among others, in windows of buildings or vehicles, meters or displays of various devices requiring transparency, it is particularly important to provide transparency together with antireflectivity.

[0003] In order to inhibit surface reflection, it is necessary to provide a low-refractive layer, as an antireflective layer, having a refractive index lower than that of the material forming the covered surface. The antireflective layer, positioned at the outermost surface, is however required to have simultaneously surface physical durability and chemical durability, and particularly, surface scratch resistance is strongly required. For this purpose, a hard coat layer is usually provided under the low-refractive layer serving as an antireflective layer.

[0004] The hard coat layer literally means a hard coating layer. A resin capable of giving a hard coating layer is

selected as a resin composing a coating composition for forming such a layer. However, a resin giving a hard coating layer has generally a high molecular weight, or has often a low solubility in a solvent because of a high density. Therefore, when forming a low-refractive layer using a coating composition for forming a low-refractive layer on a once formed hard coat layer, adhesion between the hard coat layer and the low-refractive layer tends to be insufficient. This tendency of adhesion becoming insufficient is particularly serious when forming the hard coat layer with a thermosetting resin or a coating composition containing an ionizing-radiation-setting resin as a resin component. In such a case, the low-refractive layer provided on the hard coat layer would show a considerably decreased adhesion, and this may result in a decrease in the scratch resistance or peeling of the low-refractive layer during handling.

[0005] A similar phenomenon may occur also when laminating the low-refractive layer via another layer on the hard coat layer. Between the hard coat layer and the low-refractive layer, a high-refractive layer is provided in many cases with a view to increasing the antireflectivity. This adhesion between the high-refractive layer and the low-refractive layer also tends to be lower than that between the hard coat layer and the low-refractive layer. There are

various possible lamination structures, apart from the aforementioned lamination of a high-refractive layer and a low-refractive layer, including a lamination of a medium-refractive layer, a high-refractive layer and a low-refractive layer, and the like, in terms of improving the antireflectivity. A high-refractive layer is often laminated on the final low-refractive layer. In a case where conductivity is to be imparted to the surface, a low-refractive layer may be laminated on a lamination of a conductive layer.

[0006]

[Problems to be Solved by the Invention] It is an object of the present invention to provide an antireflective member having improved adhesion between a low-refractive layer and a hard coat layer, or between a low-refractive layer and another layer, and to provide a manufacturing method permitting manufacture of such an antireflective member.

[0007]

[Means for Solving the Problems] Studies carried out by the present inventors revealed the possibility to solve the problems by adopting a lamination structure in which an impregnate portion is formed in the proximity of the interface between the hard coat layer and the low-refractive layer or between another layer present between the hard coat layer and the low-refractive layer and the low-refractive

layer. In the present invention, such an impregnate portion is formed by performing coating for forming the low-refractive layer during the lower layer formed by coating is not as yet completely set, and thus causing the coating composition thus coated to penetrate into the surface layer of the lower layer to achieve a state in which an impregnate portion is formed near the interface between the lower layer and the upper layer, and causing setting of the entire lamination, thus making it possible to achieve the foregoing lamination structure.

[0008] The first invention relates to an antireflective member having a lamination structure in which a hard coat layer and a low-refractive layer sequentially laminated which comprise a resin composition containing resins on a substrate; wherein a surface layer portion of the hard coat layer has an impregnated portion impregnated with components of the low-refractive layer. The second invention relates to an antireflective member having a lamination structure in which a hard coat layer, a high-refractive layer or a conductive layer, and a low-refractive layer sequentially laminated which comprise a resin composition containing resins on a substrate; wherein the surface layer of the hard coat has an impregnate portion impregnated with components of the high-refractive layer or the conductive layer, and/or the surface layer of the high-refractive layer or the

conductive layer has an impregnate portion impregnated with components of the low-refractive layer. The third invention relates to the first or second invention in which the hard coat layer is composed of a thermosetting resin composition containing a thermosetting resin and/or a setting resin composition comprising a set material of an ionizing-radiation-setting resin composition containing an ionizing-radiation-setting resin. The fourth invention relates to the second invention in which the high-refractive layer is composed of a thermosetting resin composition containing a thermosetting resin and/or a setting resin composition comprising an ionizing-radiation-setting resin composition containing an ionizing-radiation-setting resin. The fifth invention relates to the fourth invention in which in which the high-refractive layer further contains inorganic ultrafine particles. The sixth invention relates to any one of the first to the fifth inventions in which in which the high-refractive layer has a refractive index over 1.46. The seventh invention relates to any one of the first to the sixth inventions in which the low-refractive layer is composed of a thermosetting resin composition containing a thermosetting resin and/or a setting resin composition comprising a setting material of an ionizing-radiation-setting resin composition containing an ionizing-radiation-setting resin. The eighth invention relates to the seventh

invention in which the low-refractive layer contains a fluorine-containing polymer component. The ninth invention relates to the seventh invention in which the low-refractive layer contains a fluorine-containing oligomer component. The tenth invention relates to the seventh invention in which the low-refractive layer contains a polysiloxane component. The eleventh invention relates to any one of the first to the tenth inventions in which the low-refractive layer has a refractive index of 1.10 to 1.46. The twelfth invention relates to a manufacturing method of an antireflective member for sequentially laminating a hard coat layer and a low-refractive layer both mainly comprising a resin composition on a substrate, comprising the steps of forming a hard coat layer not as yet completely set by causing partial setting through coating of a coating composition for forming a hard coat layer containing a resin on the substrate; laminating a low-refractive layer not as yet set by coating a coating composition for forming a low-refractive layer containing a resin on the hard coat layer not as yet completely set; after lamination, forming an impregnate portion in a surface layer of the hard coat layer by causing the hard coat not as yet completely set to be impregnated with said composition for forming the low-refractive layer in said low-refractive layer not as yet set; and then, causing hardening of the entire lamination

thus formed. The thirteenth invention relates to a manufacturing method of an antireflective member for sequentially laminating a hard coat layer, a high-refractive layer and a low-refractive layer, all mainly comprising a resin composition on a substrate, comprising the steps of forming a hard coat layer by coating and causing setting of a coating composition for forming a hard coat layer containing a resin on the substrate; then, forming a high-refractive layer not as yet completely set by causing partial setting through coating of a coating composition for forming a high-refractive layer containing a resin on the hard coat layer; and thereafter, laminating an unset low-refractive layer by coating a coating composition for forming a low-refractive layer containing a resin on the high-refractive layer not as yet completely set; after lamination, forming an impregnate portion in a surface layer of the high-refractive layer by causing impregnation of the high-refractive layer not as yet completely set with the composition for forming the low-refractive layer in the unset low-refractive layer; and thereafter, causing setting of the entire lamination thus formed. The fourteenth invention relates to a manufacturing method of an antireflective member for sequentially laminating a hard coat layer, a high-refractive layer and a low-refractive layer, all mainly comprising a resin composition on a

substrate, comprising the steps of forming a hard coat layer not as yet completely set by coating and causing partial setting of a coating composition for forming a hard coat layer containing a resin on the substrate; then, laminating an unset high-refractive layer by coating a coating composition for forming a high-refractive layer containing a resin on the hard coat layer not as yet completely set; after lamination, forming a first impregnate portion in a surface layer of the hard coat layer by causing impregnation of the hard coat layer not as yet completely set with the composition for forming a high-refractive layer in the unset high-refractive layer; and further thereafter, laminating an unset low-refractive layer by coating a coating composition for forming a low-refractive layer containing a resin on the high-refractive layer not as yet completely set; after lamination, forming a second impregnate portion in a surface layer of the high-refractive layer by causing impregnation of the high-refractive layer not as yet completely set with the composition for forming the low-refractive layer in the unset low-refractive layer; and thereafter, causing setting of the entire lamination.

[0009]

[Embodiments] Fig. 1 is a sectional view illustrating a typical lamination structure of the antireflective member of the present invention. As shown in Fig. 1(a), the

antireflective member 1 of the present invention comprises a lamination structure in which, for example, a hard coat layer 3 and a low-refractive layer 4 are sequentially laminated on a substrate 2 and has an impregnate portion 5A in the surface layer (portion near the upper surface) of the hard coat layer 3, impregnated with components of the low-refractive layer. The terms "upper" and "lower" herein used mean upper and lower in the drawings. The "upper" corresponds to the observing side, and the "lower", to the opposite side.

[0010] As shown in Fig. 1(b), the antireflective member 1 of the present invention may have a lamination structure in which a hard coat layer 3, a high-refractive layer 6 and a low-refractive layer 4 are sequentially laminated on a substrate 2, and may have an impregnate portion 5B impregnated with components of the low-refractive layer in the surface layer of the high-refractive layer 6.

[0011] The impregnate portions 5A and 5B may be in a state in which only the coating composition for forming the upper layer penetrates, or in a state in which the composition penetrates and dissolves the surface layer of the lower layer, or in a state in which these two states are mixed, or it is not always necessary that the interior of the impregnate portion is uniform, having a higher degree of dissolution on the upper side and a higher degree of

penetration on the lower side. The term "impregnation" as herein used means not only a state in which all the components of the coating composition penetrate while keeping the composition ratios but also a state in which only a part of the composition penetrates.

[0012] The aforementioned lamination structure described with reference to Fig. 1(b) can have various variations. For example, the high-refractive layer 6 in the foregoing lamination structure may be replaced with two layers including a medium-refractive layer and a high-refractive layer from below, or may be replaced with another lamination structure for prevention of reflection. Or, the high-refractive layer 6 may be replaced with a functional layer having a function such as a conductive layer for imparting conductivity to the surface.

[0013] Applicable materials for the substrate 2 include a transparent resin fiber or a transparent resin sheet, a transparent resin plate (ex: acryl resin plate) and a transparent glass plate. Industrially, a transparent resin film which can be continuously worked and is flexible should preferably be used. Since the substrate 2 can be a colored transparent one for some uses, the term transparent includes colorless transparent and colored transparent ones. While the substrate 2 is transparent in many cases, the substrate is not limited to transparent ones, but may be of any state

so far as it is necessary to inhibit reflectivity.

[0014] Applicable transparent resin films or transparent resin sheets include triacetatecellulose (abbreviated as TAC, known also as cellulose triacetate), diacetatecellulose, acetatebutylatecellulose, polyethersulfon, acrylic or methacrylic, and polyurethane ones, polyesters such as polyethyleneterephthalate, cyclic polyolefins such as polycarbonate, polysulfon, polyether,, trimethylpentene, polyetherketone, (metha)acrylonitrile and trinorbornene, and those comprising thermosetting resin such as polyimide, polyamide, polyamideimide, and polysiloxane. The indication (metha) means both those having and not having metha.

[0015] A film or a sheet comprising the aforementioned thermoplastic resin is flexible and easy to use. When it is not necessary to bend at all even upon handling, and a hard one is desired, a plate-shaped one such as an aforementioned resin plate or a glass plate can be used. The substrate should preferably have a thickness of 8 to 1,000 μm when a flexible substrate is desired. For a sheet or a plate, the thickness may exceed this range. While the substrate 2 is usually flat, it may have a rugged shape or a solid shape if the substrate 2 constitutes a surface part of various articles. The substrate 2 may be subjected to various treatments for the purpose of improving adhesion on the side of lamination of the antireflective layer. The side

opposite to the side subjected to lamination of the antireflective layer may be worked to serve as a surface of various articles.

[0016] The hard coat layer 3 is provided on the substrate 2 for improving hardness of the surface of the antireflective layer of the upper layer such as the low-refractive layer. The thickness of the hard coat layer 3 should preferably be, for example, larger than 0.5 μm and smaller than 20 μm . The hard coat layer 3 may be constructed by using a relatively hard resin selected from among thermoplastic resins. It should however preferably be composed of a thermosetting resin composition containing a thermosetting resin or/and a hardened ionizing-radiation-setting resin composition (hereinafter referred to as the hardened resin composition) containing an ionizing-radiation-setting resin, or more preferably, composed of a hardened resin composition and inorganic ultrafine particles. The term the "hard coat layer" shall mean a layer prepared by coating of a coating composition, showing a surface hardness of at least H in a pencil hardness test specified in JIS K5400.

[0017] Applicable thermosetting resins include phenol resin, urea resin, dialkylphthalate resin, melamine resin, guanamine resin, unsaturated polyester resin, polyurethane resin, epoxy resin, aminoalkyd resin, melamine-urea copolycondensation resin, silicone resin, and polysiloxane

resin. These resins are used by adding, as required, crosslinking agent, polymerization initiator and other setting agents, polymerization accelerator, solvent, viscosity adjuster, or the like.

[0018] An ionizing-radiation-setting resin may, in terms of reaction energy, fall under any of photopolymerization and thermopolymerization, and in terms of the radical, under any of radical polymerization, cationic polymerization and anionic polymerization. When the resin contains an ethylene unsaturated bond, photo-radical polymerization and thermo-radical polymerization are possible, and when containing an epoxy group, thermosetting and photo-cationic polymerization is possible. Particularly, when containing an ethylene unsaturated bond, polymerization is accomplished directly by irradiation of visible light or other invisible light such as ionizing radiation (ultraviolet rays or electron beam), or indirectly under the action of the initiator. This is preferable since handling from coating to setting is easier as in the case of photo-setting.

[0019] Applicable resins containing ethylene unsaturated bond include, for example, reaction-setting polymers achieved by introducing an ethylene unsaturated bond into non-reaction polymers not having a polymeric functional group such as polyacrylic acid, polymethacrylic acid, polyacrylate, polymethacrylate, polyolefin, polystyrol,

polyamide, polyvinyl chloride, polyvinylalcohol, polyvinylbutyral, and polycarbonate.

[0020] Applicable ones containing an ethylene unsaturated bond include, for example, single-functional (metha) acrylates such as 2-hydroxyethyle (metha) acrylate, 2-hydroxypropyl (metha) acrylate, hydroxybutylacrylate, 2-hydroxy-3-phenoxypropylacrylate, carboxypolycaproatam (metha) acrylated, acrylic acid, methacrylic acid, and acrylamide; diacrylates such as ethyleneglycoldiacrylate, and pentaerithlytoldiacrylatemonostearate; triacrylates such as pentaerithlytolacrylate; multifunctional acrylates such as pentaerithlytoltriacrylate; and other radical polymeric monomers, or oligomers resulting from polymerization of these polymeric monomers. Particularly, it is desirable to use a multifunctional acrylate with a view to improving the crosslinking density.

[0021] When using a radical polymeric oligomer or monomer having an ethylene unsaturated bond, a photo-radical polymerization initiator is blended as required. Applicable photo-radical polymerization initiators include acetophenones, benzophenones, ketals, anthraquinones, thioxanthenes, azo compounds, suboxides, 2,3-dialkyldione compounds, disulfide compounds, thiuram compounds, and fluoroamine compounds. The blending ratio should preferably be 3 to 8 (weight ratio) relative to 100 of the

aforementioned radical polymeric oligomer and monomer.

[0022] Specifically, applicable photo-radical polymerization initiators include 1-hydroxyl-phenyl-ketone (made by Chiba Specialty Chemicals Co., available in a commercial name Ingacure 184), 2-methyl-1 [4-methylthio]phenyl]-2-morpholinepropane-1-on (made by Chiba Specialty Chemicals Co., available in a commercial name Ingacure 907), benzodimethylketone, 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropane-1-on, 2-hydroxy-2-methyl-1-phenylpropane-1-on, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropane-1-on, and benzophenone, applicable in combination of one or more thereof.

[0023] With the ionizing-radiation-setting resin composition and thermosetting resin composition, polysiloxane components, or more specifically, the following several types of organic reactive silicon compound may simultaneously be used. Simultaneous use of an organic reactive silicon compound permits maintenance of hardness and strength of the coated film, increases slipping property of the coated film surface, improves scratch resistance and imparts stripping property to the surface, thus providing an advantage of improving soil resistance. For any of an ionizing-radiation-setting resin composition and a thermosetting resin composition, use of a resin component into which a polar group such as a hydroxide group, a

carbonyl group, an amino group, and an amid group has been introduced is preferable since this permits formation of covalent bond with the organic reactive silicon compound and further improvement of coated film hardness and strength.

[0024] The organic silicon compound 1 can be expressed in a general formula $R_mSi(OR')_n$ where R and R' represent alkyl group having a carbon number of 1 to 10; subscript m to R and subscript n to OR' are integers each satisfying the relationship $m + n = 4$.

[0025] More specifically, applicable compounds include tetramethoxysilane, tetraethoxysilane, tetra-iso-propoxysilane, tetra-n-propoxysilane, tetra-n-butoxysilane, tetra-sec-butoxysilane, tetra-tert-butoxysilane, tetrapentaethoxysilane, tetrapenta-iso-propoxysilane, tetrapenta-n-propoxysilane, tetrapenta-n-butoxysilane, tetrapenta-sec-butoxysilane, tetrapenta-tert-butoxysilane, methyltriethoxysilane, methyltripropoxysilane, methyltributoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, dimethylethoxysilane, dimethylmethoxysilane, dimethylpropoxysilane, dimethylbutoxysilane, methyldimethoxysilane, methyldiethoxysilane, and hexyltrimethoxysilane.

[0026] Organic silicon compound 2 which can be simultaneously used with ionizing-radiation-setting resin composition and thermosetting resin composition is a silane

bonding agent.

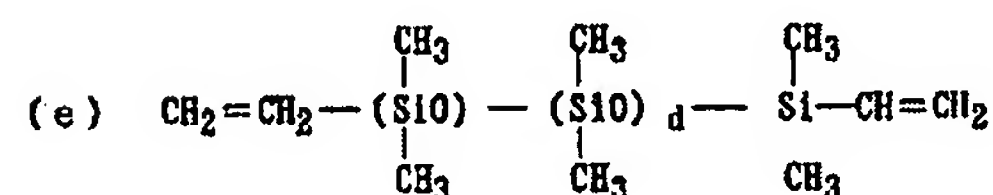
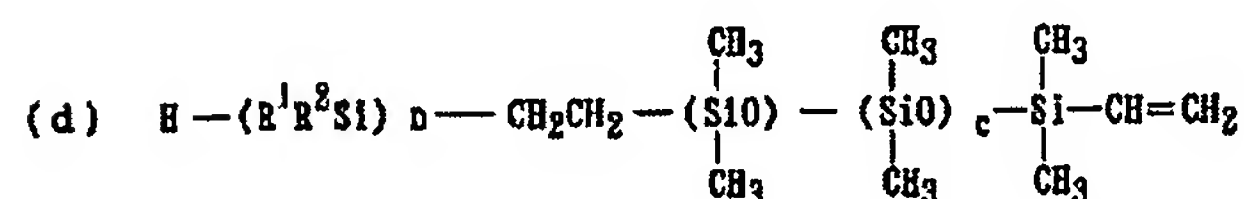
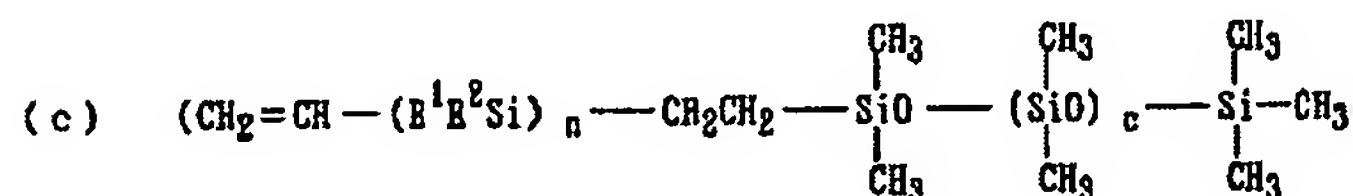
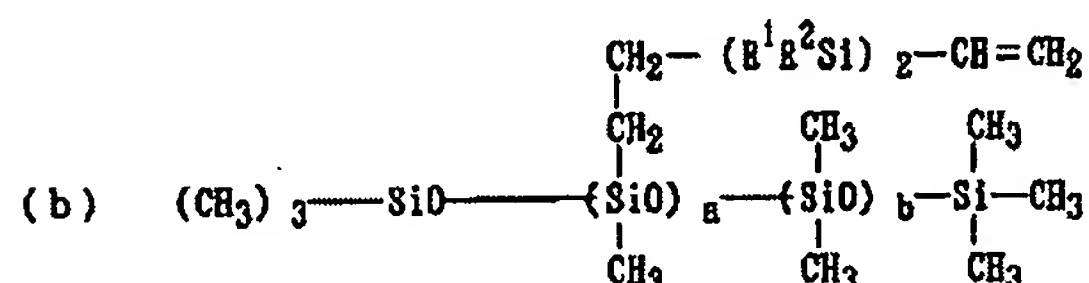
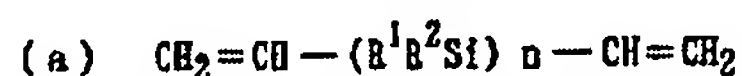
[0027] More specifically, applicable organic silicon compounds 2 include γ -(2-aminoethyl) aminopropyltrimethoxysilane, γ -(2-aminoethyl) aminopropylmethyldimethoxysilane, β -(3,4-epoxycyclohexyl) ethyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -methacryloxypropylmethoxysilane, N- β -(N-vinylbenzylaminoethyl)- γ -aminopropylmethoxysilane·chlorate, γ -glycidoxypropyltrimethoxysilane, aminosilane, methylmethoxysilane, vinyltriacetoxysilane, γ -mercaptopropyltrimethoxysilane, hexamethyldisilazane, vinyltris(β -methoxyethoxy)silane, octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride, methyltrichlorosilane, and dimethyldichlorosilane.

[0028] Organic silicon compound 3 which can be used simultaneously with ionizing-radiation-setting resin composition and thermosetting resin composition is an ionizing-radiation-setting silane compound. Specifically, applicable organic silicon compounds 3 include a plurality of functional groups which react to irradiation of ionizing radiation and conduct crosslinking, for example, an organic silicon compound having a polymerous double bond group and having a molecular weight smaller than 5,000. More specifically, they include vinyl functional polysilane, and vinyl functional polysilane available from reaction of

single-terminal functional polysilane, double-terminal vinyl functional polysilane, single-terminal vinyl functional polysiloxane, double-terminal vinyl functional polysiloxane, and compounds thereof. Further more specifically, there are available the following compounds:

[0029]

[Chemical Formula 1]



In the above-mentioned formulae (a) to (e), R^1 and R^2 represent an alkyl group having a carbon number of 1 to 4, and a to d and n are values leading to a molecular weight smaller than 5,000.

[0030] Urethaneacrylate, particularly, polyurethaneacrylate may be used simultaneously with ionizing-radiation-setting resin composition and thermosetting resin composition. In

general, especially multifunctional acrylates, while giving a coated film with an excellent hardness, has a deficiency of a low impact resistance of the coated film which becomes brittle. Addition of polyurethaneacrylate improves impact resistance, tending to impart flexibility to the coated film. A polymer into which (meth)acryloyl group has been introduced or a polymer of silicone resin can be preferably used within a range not impairing the physical properties of the hard coat thin layer 4. The hard coat layer 3, which can be formed with the aforementioned resin compounds as main components, should more preferably further contain inorganic ultrafine particles.

[0031] The hard coat layer 3 can be formed, apart from the above-mentioned components, through coating by use of a hard coat layer forming coating composition prepared by adding, as required, a solvent, a UV shielding agent, a UV absorbing agent, a surface adjusting agent (leveling agent), or other additives. For coating, any of the roll coating method, the gravure coating method, the slide coating method, the spray coating method, the dip coating method and the screen printing method is applicable, and after coating, the hard coat layer 3 can be formed by drying, heating or irradiation of ultraviolet rays or electron beam for setting.

[0032] The low-refractive layer 4 comprises a resin composition formed by coating using a low-refractive layer

forming coating composition containing an appropriate coating transparent resin and low-refractive particles, preferably ultrafine particles. Or, the low-refractive layer 4 comprises a resin composition formed by using a coating composition prepared with or without inorganic particles or inorganic ultrafine particles, containing a low-refractive resin component having itself a low refractive index.

[0033] Applicable low-refractive inorganic particles or inorganic ultrafine particles include, for example, LiF, MgF_2 , $3\text{NaF} \cdot \text{AlF}_3$ and AlF_3 (all having $n=1.4$), Na_3AlF_6 (cryolite; $n=1.33$) and SiO_x ($1.50 \leq x \leq 2.00$), $n=1.35$ to 1.48). A coating composition is prepared by use of particles or ultrafine particles selected from among these compounds is coated onto the substrate 2, and solidified through drying, thus forming a low-refractive layer 4. Applicable low-refractive particles or ultrafine particles include, for example, a fluororesin or a silane resin, used singly, and resin particles containing these resins. These resins can be used preferably only if the refractive index is within a range of 1.30 to 1.46 .

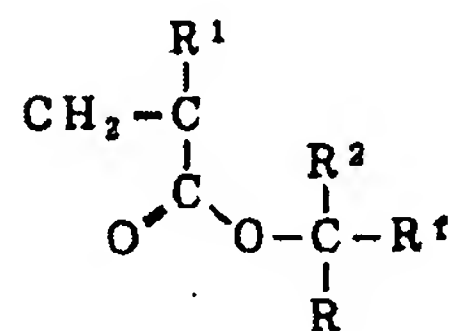
[0034] However, the refractive index of commonly used transparent resins for coating is not very low. More preferably, therefore, a low-refractive layer 4 should be formed by the use of a coating composition prepared with a

fluorine-containing polymer or a fluorine-containing oligomer as a resin component, in order to achieve a low refractive index. The above-mentioned polysiloxane component may be contained.

[0035] A fluorine-containing polymer or a fluorine-containing oligomer is obtained through polymerization or copolymerization of a fluorine-containing monomer having an ethylene unsaturated bond. Applicable fluorine-containing monomers having an ethylene unsaturated bond include fluoroolefins such as fluoroethylene, vinylidene fluoride, tetrafluoroethylene, hexafluoropropyleneethylene, perfluorobutadiene, and perfluoro-2,2-dimethyl-1,3-dioxol, alkyl, alkenyl and allylester obtained through complete or partial fluorination of acrylic acid or methacrylic acid (represented by the following "Chemical Formula 2" or "Chemical Formula 3"), and further, completely or partially fluorinated vinylethers, completely or partially fluorinated vinylesters, and completely or partially fluorinated vinylketone.

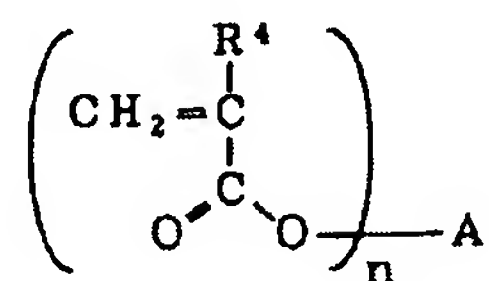
[0036]

[Chemical Formula 2]



[0037]

[Chemical Formula 3]



[0038] In the foregoing Chemical Formula 2, R¹ represents a hydrogen atom, alkyl group having a carbon number of 1 to 3, or a halogen atom; R^f represents a completely or partially fluorinated alkyl group, alkenyl group, hetero group, or allyl group; R² and R³ represent, independently of each other, a hydrogen atom, alkyl group, alkenyl group, hetero group, allyl group, or a group defined by the aforementioned R^f; R¹, R², R³, and R^f may have respectively a substituent other than a fluorine atom; and two or more arbitrary groups bonded with each other may form a cyclic structure with R², R³ and R^f.

[0039] In the foregoing Chemical Formula 3, A represents a completely or partially fluorinated organic group of a value n; R⁴, a hydrogen atom, an alkyl group having a carbon number of 1 to 3, or a halogen atom; R⁴ may have a substituent other than a fluorine atom; and n, an integer of 2 to 8.

[0040] Combination of a fluorine-containing polymer, a fluorine-containing monomer and/or oligomer having mutually polymerizable polymeric functional groups is desirable

since it permits improvement of film-formability of a coating composition for coating under the effect of the fluorine-containing polymer, and at the same time, improvement of the crosslinking density and coating adaptability under the effect of the fluorine-containing monomer and/or oligomer, the balance of these components permitting achievement of satisfactory hardness and strength of the coated film. Particularly, by using a combination of a fluorine-containing polymer having a number average molecular weight of 20,000 to 100,000 and a fluorine-containing monomer and/or oligomer having a number average molecular weight smaller than 20,000, it is easy to take balance of various physical properties including coating adaptability, film formability, film hardness and film strength. This combination is therefore more preferable. When the refractive index of the fluorine polymer is sufficiently low, combination with a monomer and/or an oligomer not containing fluorine is more preferable since it is easier to improve the film strength. Applicable monomers and oligomers not containing fluorine include having an ethylene unsaturated bond, which have previously been pointed out as materials for composing a hard coat layer 3.

[0041] As a fluorine-containing monomer or oligomer as described above, a single monomer or a copolymer comprising one or more selected from the above-mentioned fluorine-

containing monomers, or a copolymer with one or more monomers not containing fluorine can be used. In order to improve mechanical strength of the low-refractive layer 4, it is effective to improve the adhesion between the low-refractive layer 4 and the lower layer. For this purpose, any of the resin components composing the low-refractive layer forming the coating composition should preferably contain a polar group such as a hydroxide group, a carboxyl group, an amino group or an amide group introduced therein.

[0042] A fluorine-containing monomer not containing a polymerous functional group is also applicable. More specifically, applicable ones include polytetrafluoroethylene, 4-fluoroethylene-6-fluoropropylene copolymer, 4-fluoroethylene-per-fluoroalkylvinylether copolymer, 4-fluoroethyleneethylene copolymer, polyvinylfluoride, polyvinylidene fluoride, a polymer or a copolymer of alkylalkenyl, or allylester resulting from complete or partial fluorination of acrylic acid or methacrylic acid (for example, the foregoing "Chemical Formula 2" or "Chemical Formula 3"), fluoroethylene-hydrocarbon vinylether copolymer, and fluorine denatured epoxy, polyurethane, cellulose-based, phenol, polyimide, and silicone resins. Apart from the above, amorphous transparent fluororesin (made by Asahi Glass Co.; commercial name: "SAITOP") and the like are also applicable.

[0043] When forming a low-refractive layer 4 by the use of a coating composition prepared with the aforementioned fluorine-containing polymer or fluorine-containing oligomer as a resin component, the particles having a low refractive index as described above can be used. With a view to ensuring a higher transparency, it is more preferable to add ultrafine particles.

[0044] An ultrafine particle as herein used is smaller than a particle generally known as a fine particle having a particle diameter from several μm to several hundred μm . Specifically, the particle diameter of the ultrafine particle used in the present invention, varying with the optical performance required by the particular use, is therefore difficult to specify in a general term, should preferably be within a range from 1 nm to 500 nm. Use of a primary particle diameter under 1 nm does not lead to improvement of hardness and strength of the film. A primary particle diameter over 500 μm impairs transparency of the film, and for some uses, is not applicable at all. The ultrafine particle may be of any shape such as spherical or needle shape so far as it is uniformly dispersible in resin and can ensure satisfactory film hardness and strength.

[0045] Using a fluorine-containing polymer or a fluorine-containing oligomer as a resin component, a low-refractive layer 4 can be formed by coating by the use of a low-

refractive layer forming coating composition prepared by blending a photoradical polymerization initiator as required, and adding, also as required, a solvent, a UV shielding agent, a UV absorbent, a surface adjuster (leveling agent), or other additives. Applicable coating methods include the roll coat method, the gravure coat method, the sliding coat method, the spray coat method, the dip coat method and the screen printing method. After coating, the film is set by drying, warming or heating as required, or subjected to irradiation of ultraviolet rays or electron beam. The low-refractive layer 4 should preferably have a refractive index of 1.10 to 1.46 and a thickness of 3.0 to 200 nm.

[0046] In the presence of the high-refractive layer 6 described above with reference to Fig. 1(b), the high-refractive layer 6 should preferably have a refractive index of 1.46 to 1.90 and a thickness of 50 to 200 nm.

[0047] The high-refractive layer 6 contains the same resin components as those for forming the hard coat layer 3, and is formed by using, in addition to these resin components, a high-refractive layer forming coating composition in which inorganic fine particles for achieving a high refractive index of the layer 6, preferably, inorganic ultrafine particles are blended. As the resin components, those having a high hardness are used from among thermoplastic resins, or more preferably, a thermosetting resin or an

ionizing-radiation-setting resin is used. These resin components set, and formation of this layer 6 can be accomplished in a manner similar to that of the hard coat layer 3.

[0048] As the inorganic fine particles, or preferably, the inorganic ultrafine particles, materials having a high refractive index are applicable. These materials include titania (refractive index $n = 1.9$ to 2.3), zirconia ($n = 1.6$ to 2.0) zinc oxide ($n = 1.6$ to 2.0), alumina ($n = 1.5$ to 1.7), tin oxide ($n = 1.7$ to 2.0), indium-doped tin oxide ($n = 1.6$ to 1.9), antimony-doped tin oxide (= ATO; $n = 1.6$ to 1.9), and aluminum-doped zinc oxide (= AZO; $n = 1.7$ to 2.0). These materials are applicable so far as the refractive index is within a range required by the hard coat layer 4. When these high-refractive inorganic fine particles or the inorganic ultrafine particles are conductive, the high-refractive layer 6 can serve as a conductive layer which is desirable since this imparts conductivity to the surface layer of the antireflective layer, and hence to the antireflective member, permitting imparting antistatic performance as a result.

[0049] As described schematically above by citing Figs. 1(a) and (b), the antireflective member 1 of the present invention has an impregnate portion 5A (or 5B) having components of the low-refractive layer in the surface layer

of the hard coat layer 3 or in the surface layer of the high-refractive layer 6. The impregnate portion 5A or 5B is formed as follows.

[0050] The case described with reference to Fig. 1(a) above will now be described with reference to Fig. 2. To begin with, coating is conducted by the use of a hard coat forming coating composition on a substrate 2 shown in Fig. 2(a), and the coat is set through appropriate means. A not as yet completely set hard coat layer 3p ("p" as used here is the initial of "partial" meaning that this is partial setting) is formed by discontinuing setting during the stage of "partial setting" (Fig. 2(b)).

[0051] Coating is applied by the use of a low-refractive layer forming coating composition on the not as yet completely set hard coat layer 3p to form an unset low-refractive layer 4a at this point in time (Fig. 2(c)). The subscript a means that the layer is unset. By waiting for the lapse of some time without taking any action for setting immediately after coating, the lower hard coat layer 3p is caused to be impregnated with the low-refractive layer forming coating composition in the unset low-refractive layer 4a to form an impregnate portion in the surface layer of the not as yet completely set hard coat layer 3p. Therefore, the extent of partial setting of the lower hard coat layer 3p, and the viscosity and chemical affinity

imparting impregnability of the low-refractive layer forming coating composition are selected so as to ensure appropriate impregnation.

[0052] At the point in time when impregnation progresses to some extent, by completely setting the entire layer, i.e., by completely setting the hard coat layer 3p serving as the lower layer including the impregnate portion and the unset low-refractive layer 4a serving as the upper layer, the hard coat layer 3 and the low-refractive layer 4 are laminated on the substrate 2, thus permitting obtaining an antireflective member 1 (Fig. 2(d)) having the set impregnate portion 5A in the surface layer of the hard coat layer 3. Not only the hard coat layer 3 and the low-refractive layer 4 have laminated with each other, but also have a portion of the hard coat layer 3 impregnated with the low-refractive layer forming coating composition used when forming the low-refractive layer, thus resulting in a state of lamination in which the hard coat layer 3 and the low-refractive layer 4 are strongly bonded.

[0053] As described above with reference to Fig. 1(b), when the high-refractive layer 6 is present and the surface layer of the high-refractive layer 6 has an impregnate portion 5B impregnated with the components of the low-refractive layer, the foregoing method is applicable. As described with reference to Fig. 1(b), when only the surface layer of the

high-refractive layer 6 has the impregnate portion 5B, operation can be conducted in a similar manner as above by replacing the hard coat 3 in the above description with the high-refractive layer 6.

[0054] When there is present a high-refractive layer 6, the impregnate portion may be produced also from the relationship between the hard coat layer 3 and the high-refractive layer 6. In this case, the hard coat layer 3 is caused to partially set in a not as yet completely set state in advance. The first impregnate portion is formed after coating the high-refractive layer forming coating composition, by impregnating the lower layer during unset state, thus forming a first impregnate portion. Thereafter, a setting action is taken to cause partial setting up to a state in which at least the high-refractive layer 6 is not as yet completely set. At this point in time, the hard coat layer 3 serving as the lower layer may be completely set, or may be in a state not as yet completely set. Subsequently, the low-refractive layer forming coating composition is coated, and a second impregnate portion is formed by impregnating the lower layer with the coating composition during the period the layer is not as yet set. Finally, a setting action is taken to achieve complete setting of the entire lamination, thereby completing an antireflective member 1 in which the surface layer of the hard coat layer 3

and the surface layer of the high-refractive layer 6 have respective set impregnate portions, this intensifying adhesion between the high-refractive layer 6 and the low-refractive layer 4.

[0055] In the above description, a state in which setting is not as yet completed is achieved by varying the time of setting action, conditions, and the total amount of energy imparted to the film on the basis of the condition for complete setting including drying, warming, heating, irradiation of UV-rays or electron beam used for setting. In a typical case, if the condition for complete setting by irradiation of UV-rays in an amount of irradiated rays of 80 to 2000 mJ/cm², achievement of a half-cure state in which the layer is not as yet completely set, the amount of irradiation should be about 5 to 80 mJ/cm² which is several % to several tens of % of the amount of irradiation for complete setting.

[0056]

[Examples] (Example 1) A hard coat layer forming composition of the following chemical composition was prepared and subjected to bar coating on a triacetylcellulose film having a thickness of 80 μm, and dried. After removing the solvent, partial setting was performed using an ultraviolet-rays irradiator (made by Fusion UV System Japan Co.; source: H-Bulb), under

conditions including an amount of irradiation of 20 mJ/cm² to form a transparent hard coat layer having a thickness of 4 μm, thus obtaining a hard coat film. The number and the blending ratio were based on the weight.

(Hard coat layer forming composition)

- Pentaerythritoltetraacrylate: 20.0 parts
- Photopolymerization initiator: 1.0 part

(made by Chiba Specialty Chemicals Co.; commercial name: Irgacure 184)

- Methylisobutylketone: 80 parts

[0057] A fluorine-based UV-setting type coating composition (made by JSR; commercial name: OPSTAR JM5010) was bar-coated onto the thus formed hard coat layer, dried, and the solvent was removed. Then, setting was accomplished by irradiating UV-rays by the use of a UV irradiator similar to that used above, under conditions including an amount of irradiation of 300 mJ/cm² to form a low-refractive layer having a refractive index of 1.41, thus obtaining an antireflective film. When measuring the reflectance by using a spectrophotometer (made by Shimazu Seisakusho), the thickness of the low-refractive layer was set so that the minimum value of reflectance was near a wavelength of 550 nm.

[0058] (Example 2) A hard coat film was obtained through complete setting in the same manner as in Example 1 except that an amount of UV irradiation of 100 mJ/cm² was used. A

high-refractive layer forming composition to be coated onto the hard coat layer of the above-mentioned hard coat film was obtained by shaking the following components except for the photoinitiator with zirconia beans (diameter: 0.3 mm) in an amount of about four times as large as a medium in a paint shaker for 10 hours, and after shaking, adding the photoinitiator.

[0059]

(high-refractive layer forming coating composition)

- Rutile type titanium oxide: 10 parts
(made by Ishihara Industry Co.; product No.: TT051(C);
primary particle diameter: 0.01 to 0.03 μm)
- Pentaerythritoltriacylate: 4 parts
(made by Nippon Chemicals Co.; commercial name: PET30)
- Dispersant: 2 parts
(made by Bic-Chemie Japan Co.; DISPERBIC 163)
- Photoinitiator: 0.2 parts
(made by Chiba Specialty Chemicals Co.; commercial name:
IREGACURE 184)
- Methylirobutylketone: 37.3 parts

[0060] The aforementioned high-refractive layer forming composition was coated onto the hard coat layer of a hard coat film in the same manner as in forming the hard coat layer. Provided however that partial setting was caused with an UV irradiation amount of 20 mJ/cm². The thickness

of the high-refractive layer was set so that the minimum value of reflectance was near a wavelength of 550 nm upon measuring the reflectance by use of a spectrophotometer (made by Shimazu Seisakusho).

[0061] A low-refractive layer was formed on the thus formed high-refractive layer using the same composition by the same method as in Example 1. In this Example as well, the thickness of the high-refractive layer was set so that the minimum value of reflectance is near a wavelength of 550 nm upon measuring the reflectance by use of a spectrophotometer (made by Shimazu Seisakusho C.)

[0062] (Comparative Example 1) An antireflective film was prepared in the same manner as in Example 1 except that an amount of UV irradiation of 300 mJ/cm² was used upon forming the hard coat layer.

[0063] (Comparative Example 2) An antireflective film was prepared in the same manner as in Example 3 except that an amount of UV irradiation of 150 mJ/cm² was used upon forming the high-refractive layer. An antireflective film was similarly prepared.

[0064] The thus obtained antireflective films of the Examples and the Comparative examples were evaluated as to three items including reflectance, film strength, and adhesion. The reflectance is the one measured with spectrophotometer (made by Shimazu Seisakusho) at a

wavelength of 550 nm. The reflectance should preferably be lower than 1.2%. The film was rubbed 20 times under a certain load with steel wool #0000, and measurement was performed by a turbidimeter (made by Nippon Denshoku; commercial name: NDH2000). The mass (unit: g) of the weight of the load value at the moment when Haze varied was recorded as the film strength. In uses in which human hands tend to easily touch the film, the film strength should preferably be higher than 200 g. Even film strength lower than 200 g is allowable if the frequency of human touch is low. The adhesion was evaluated through a checkered peeling test by means of a cellophane tape.

[0065]

[Table 1]

Evaluated item Sample	Reflectance (%)	Film strength (g)	Adhesion
Example 1	0.86	1000	No peeling
Example 2	0.18	1000	No peeling
Comparative Example 1	0.90	100	Partial peeling
Comparative example 2	0.20	100	Partial peeling

[0066]

[Advantages] According to the invention of claim 1, the hard coat layer serving as the lower layer is impregnated with the components of the low-refractive layer serving as the upper layer. It is therefore possible to provide an antireflective member having an improved adhesion between

these layers. According to the invention of claim 2, the hard coat layer, the high-refractive layer or the conductive layer, and the low-refractive layer are laminated, and impregnation of the lower layer with the components of the upper layer in one or two interfaces of these layer makes it possible to provide an antireflective member having an improved adhesion between the two layers at corresponding position. According to the invention of claim 3, the hard coat layer is composed of a thermosetting resin and/or an ionizing radiation-setting resin in addition to the advantages of claim 1 or 2. It is therefore possible to provide an antireflective member having a higher adhesion and a higher surface hardness. According to the invention of claim 4, the high-refractive layer is composed of a thermosetting resin and/or an ionizing-radiation-setting resin in addition to the advantage of the invention of claim 2. It is therefore possible to provide an antireflective member having a higher adhesion and a higher surface hardness. According to the invention of claim 5, further containing inorganic ultrafine particles improves the reflectance of the high-refractive layer in addition to the advantage of the invention of claim 4. It is therefore possible to provide an antireflective member having a further improved antireflectivity. According to the invention of claim 6, the reflectance of the high-refractive

layer is regulated in the invention of any one of claim 1 to 5. It is therefore possible to provide an antireflective member which can reliably display the antireflectivity. According to the invention of claim 7, the low-refractive layer is composed of a thermosetting resin and/or an ionizing-radiation-setting resin, thus improving the hardness of the low-refractive layer, in addition to the advantage of any one invention of claims 1 to 6. According to the invention of claim 8, it is possible to provide an antireflective member having a lower refractive index of the low-refractive layer, and a higher antireflectivity, in addition to the advantage of the invention of claim 7. According to the invention of claim 9, it is possible to provide an antireflective member which has a lower refractivity index of the low-refractive layer, a higher antireflectivity, and a higher surface hardness resulting from the hardness of the low-refractive layer, in addition to the advantage of the invention of claim 7. According to the invention of claim 10, it is possible to provide an antireflective member having an improved soil resistance since the slippage of the low-refractive layer surface is improved, with an improved scratch resistance and stripping property is imparted to the surface, in addition to the advantage of the invention of claim 7. According to the invention of claim 11, it is possible to provide an

antireflective member in which a reliable antireflectivity is achievable, since the refractive index of the low-refractive layer is regulated, in addition to the advantage of the invention of any one of claims 1 to 10. According to the invention of claim 12, it is possible to provide a manufacturing method of an antireflective member permitting improvement of adhesion between the hard coat layer and the low-refractive layer, since, upon sequentially laminating the hard coat layer and the low-refractive layer, the upper layer is formed in a state in which the lower layer is partially set to impregnate the lower layer with the components of the upper layer. According to the invention of claim 13, it is possible to provide a manufacturing method of an antireflective member which permits improvement of adhesion between layers, upon sequentially laminating the hard coat layer, the high-refractive layer and the low-refractive layer, by forming the upper layer in a state in which the lower layer is set and the middle layer is partially set, to cause the middle layer to be impregnated with the components of the upper layer. According to the invention of claim 14, it is possible to provide a manufacturing method of an antireflective member permitting improvement of adhesion between the hard coat layer and the high-refractive layer and between the high-refractive layer and the low-refractive layer, upon sequentially laminating

the hard coat layer, the high-refractive layer, and the low-refractive layer, by forming the middle layer in a state in which the lowermost layer is partially set, to impregnate the lowermost layer with the components of the middle layer, thus improving adhesion between these layers, and by forming the upper layer in a state in which the middle layer is partially set, to impregnate the middle layer with the components of the upper layer, thus improving adhesion between these layers.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a sectional view illustrating the antireflective member of the present invention.

[Fig. 2] Fig. 2 is a sectional view illustrating the process of manufacturing of the antireflective member of the present invention.

[Reference Numerals]

- 1: Antireflective member
- 2: Substrate
- 3: Hard coat layer
- 4: Low-refractive layer
- 5: Compatible portion
- 6: High-refracdtive layer